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Wastewater Treatment from Heavy Metal Ions, Based on the Physico– Chemical Processes. Review

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Abstract:

In this paper, we present an overview of modern technologies used for the treatment of wastewater containing heavy metal ions. Special attention is given to physico– chemical methods. We provide a detailed examination of treatment techniques using coagulants and flocculants, as well as sorption, ion– exchange, and electrochemical processes. For each method, we have identified the key advantages and disadvantages. Electrochemical methods have proven to be efficient and promising technologies. The equipment used for these processes is compact and highly productive. Moreover, the operation and management of such systems are relatively easy to automate. The most common electrochemical methods include electrocoagulation, electroflotation, and galvanocoagulation. In conclusion, we emphasize the need for further research to develop new wastewater treatment technologies and to improve existing methods by intensifying physico– chemical processes.80 sources.

Keywords: coagulation; flocculation; adsorption; ion exchange; electrocoagulation; electroflotation; galvanic coagulation; heavy metal ions.

INTRODUCTION

Today, humanity is facing a serious global water crisis. Two billion people around the world do not have access to safe drinking water, and 3.6 billion people—almost half of the global population—use sewage systems that do not properly treat waste. These staggering figures were released today by the World Health Organization (WHO) and the United Nations Children's Fund (UNICEF) to coincide with the start of the historic Water Conference—the first of its kind in nearly 50 years[1-3].

Millions of children and families lack access to adequate sanitation and hygiene products, even something as basic as soap. The consequences can often be deadly. Every year, at least 1.4 million people—many of them children—die from preventable causes related to unsafe water and poor sanitation. For example, cholera is now spreading in countries that have not had an outbreak in decades[4-6].

Water scarcity primarily threatens public safety and health. Against the backdrop of increasing scarcity, the demand for water rises each year. Over the past 15 years, the amount of water per person in Uzbekistan has decreased by 48%, from 3,048 cubic meters in 2008 to 1,589 cubic meters by the end of 2022.

Despite this reduction, water consumption in Uzbekistan remains significantly higher than in countries like Egypt, Germany, Israel, Bahrain, and the UK. Uzbekistan is currently among the top 30 countries facing severe water stress, ranking 25th out of 164 countries. Experts predict that by 2030, Uzbekistan may face a fresh water deficit of 7 billion cubic meters—equivalent to the volume of four Charvak reservoirs or nearly two Tuzkan lakes. By 2050, this deficit could double.

Climatic and anthropogenic changes over the past 50 years have led to a 20% reduction in the volumes of Uzbekistan's key rivers, the Syr Darya and Amu Darya. This has resulted in dust storms and droughts, further worsening the problem of water scarcity. It is crucial to regularly remind the public about the growing problem of deteriorating water quality[7-10].

The main pollutants in the wastewater from machine– building enterprises, as well as non– ferrous metallurgy and instrument– making industries, include heavy metal ions. Heavy metals are among the priority pollutants that must be monitored in all environments. Special attention is paid to those metals that have the most significant environmental impact due to their widespread use in industry and their ability to accumulate in the ecosystem, posing serious risks due to their biological activity and toxicity. These metals include nickel (II), chromium (III) and (VI), zinc (II), copper (II), cadmium (II), and others.

Modern methods for effectively treating wastewater from various pollutants, including heavy metal ions, rely heavily on physicochemical technologies. The improvement and expanded application of these methods have enabled the development of complex technological processes with functional specialization at different stages. Currently, physicochemical technologies are widely used to treat both natural and wastewater, offering significant advantages in addressing environmental protection challenges [11-14].

Methods and materials.

Wastewater Treatment Using Coagulants and Flocculants

Wastewater treatment using coagulants and flocculants is widely employed among physicochemical methods [15]. Commonly used coagulants include aluminum salts, iron salts, or their mixtures. The most frequently used coagulants for treating wastewater containing heavy metal ions are aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$), sodium aluminate ($NaAlO_2$), aluminum hydroxochloride ($Al(OH)_5Cl$), and aluminum– potassium or aluminum– ammonium tetraoxosulfates (also known as alum and ammonium alum) [16]. Of these, aluminum sulfate and sodium aluminate are the most common.

Aluminum sulfate is effective within the pH range of 5 to 7.5, dissolves well in water, and is relatively inexpensive. It is typically used in either dry form or as a 50% solution. Sodium aluminate, on the other hand, is used in dry form or as a 45% solution. As an alkaline reagent, it forms rapidly precipitating flocs at a pH of 9.3– 9.8. In many cases, a mixture of $NaAlO_2$ and $Al_2(SO_4)_3$ is utilized. The combined use of these salts enhances the clarification effect, increases the density and speed of floc sedimentation, and expands the optimum pH range for the treatment process.

Aluminum oxychloride is less acidic than the aforementioned coagulants and is therefore suitable for treating slightly alkaline waters [17].

The salt composition of the water significantly influences the coagulation process. Anions of weak acids contribute to the buffer capacity, aiding in the hydrolysis of the coagulant. Cations, on the other hand, can alter the charge of colloidal particles. For instance, in hard water, negatively charged colloids can acquire a positive charge due to the adsorption of calcium and magnesium ions. At pH values above 7, this charge can be neutralized by SO_4^{2-} ions from aluminum sulfate, and the aluminum ion will fully hydrolyze to $Al(OH)_3$. In this case, the required dose of coagulant will be lower than for treating negatively charged particles. Therefore, the partner ion SO_4^{2-} plays a significant role in the coagulation process in waters with high hardness. When a coagulant is added to water, it causes the particles to undergo compression of the electric double layer, bringing them close enough for intermolecular forces of attraction to come into play, leading to particle aggregation.

Among iron salts, the most commonly used coagulants for treating wastewater containing heavy metal ions are iron sulfates ($Fe_2(SO_4)_3 \cdot 2H_2O$, $Fe_2(SO_4)_3 \cdot 3H_2O$, $FeSO_4 \cdot 7H_2O$) and ferric chloride ($FeCl_3$). The best purification results are achieved using trivalent iron salts [17].

However, iron salts have several disadvantages compared to aluminum salts:

1. When iron cations react with some organic compounds, strongly staining soluble complexes can form.
2. The strong acidic properties of iron increase the corrosion of equipment.
3. Iron hydroxide forms flocs with a less developed surface area [18].

The use of mixed coagulants, which combine aluminum and iron compounds, results in improved water treatment efficiency. Literature reviews indicate that iron– aluminum coagulants offer several advantages over those containing only one metal. The broader optimum pH range is attributed to the diverse hydrolysis products, and the faster sedimentation of flocs is due to a denser packing of particles, resulting in more efficient treatment [19].

Recently, a new, highly effective titanium coagulant has gained popularity. This titanium reagent allows for the complete purification of wastewater from galvanic production processes, effectively removing organic compounds, while achieving a 50– 67% reduction in heavy metal ion concentration.

In addition to the coagulants mentioned, various clays, aluminum– containing industrial wastes, pickling solutions, pastes, and slags containing silicon dioxide can also be used for wastewater treatment.

The primary purpose of flocculants is to enhance the coagulation process [20]. Natural flocculants include starch, dextrin, esters, cellulose, and similar compounds. Active silica is the most commonly used inorganic flocculant. Among synthetic organic coagulants, polyacrylamide $[-CH_2-CH-CONH_2]_n$, technical polyacrylamide (PAA), and hydrolyzed polyacrylamide (HPPA) are widely used. During wastewater treatment with flocculants, micelles of heavy metals are formed, which may carry either positive or negative charges. A wide variety of polyelectrolytes are employed to form micelles during flocculation. However, preference is generally given to cationic and amphoteric polyelectrolytes, as heavy metal micelles are primarily negatively charged.

Recently, composite reagents, consisting of individual ingredients that act as coagulants, flocculants, precipitants, and adsorbents, have gained popularity. Examples of such composite reagents include aluminosilicon coagulant– flocculant AKFC and silox. The use of these composites simplifies reagent management in local treatment facilities, reduces energy consumption, and decreases the footprint of treatment plants.

The introduction of water treatment processes using coagulants and flocculants represents a significant advancement in treatment technology. However, as water quality standards continue to rise, some notable disadvantages of these technologies have become apparent.

A common drawback of all water treatment methods involving coagulants and flocculants is that the technological operation of treatment facilities becomes unregulated when the water quality at the source fluctuates. The low efficiency of treatment plants in many cases is due to the inherent challenges of the coagulation process itself: slow hydrolysis of the coagulant and low floc formation rates at lower temperatures; insufficient floc strength, leading to the loss of contaminants from the filter medium and the breakdown of sludge in clarifiers; and the low density of flocs formed during the coagulation of colored water [21].

Sorption Methods for Wastewater Treatment

Sorption methods of wastewater treatment are not only highly efficient but also among the most environmentally friendly. The primary criterion for selecting a material for wastewater pretreatment is its sorption properties, porous structure, and cost– effectiveness. Carbon sorbents, silica, peat and its derivatives, ashes, and carbonate– containing anthropogenic wastes [22] are recognized as some of the most popular materials for treating wastewater containing heavy metal ions.

Various grades of activated carbon sorb heavy metal ions with different absorption capacities. The main factor determining sorption efficiency is the pH value. The maximum sorption capacity is achieved at a pH of 4, meaning the process occurs before the formation of hydrolysis products. Granulated activated carbon saturated with nitrohumic acid has a particularly high absorption capacity for heavy metal ions. For additional treatment of wastewater containing heavy metal ions at initial concentrations up to 10 mg/L, starch xanthogenates are considered very promising reagents [23].

Coal obtained by the combustion of solid organic waste, particularly waste from sugarcane production, as well as hydrolyzed lignin, also possesses the ability to sorb heavy metal ions from solutions. High efficiency in the treatment of wastewater containing lead (II) ions can be achieved using modified basalt sorbents[24].

Sorption methods are economically advantageous only when the sorbents are used repeatedly. However, after the regeneration of sorbents, a large quantity of highly toxic and concentrated eluates is produced, which requires additional neutralization and disposal. Furthermore, the disposal of spent sorbent material presents a significant challenge. As a result, treatment methods based on ion exchange, utilizing both natural and synthetic materials, are gaining increasing attention. These methods not only allow for the extraction of heavy metal ions from wastewater but also enable the reuse of treated wastewater in recycling processes for water supply systems[25].

Results and discussion.

The Tuzkan storage lake, like many other artificial reservoirs, serves as a significant repository for wastewater. Understanding the chemical composition of this water body is critical for evaluating its environmental impact, wastewater treatment efficacy, and future water quality management strategies. In this study, the chemical properties of the Tuzkan storage lake's wastewater were analyzed, revealing a range of important indicators. The pH of the water was recorded at 8.2, indicating slightly alkaline conditions. This pH level falls within an acceptable range for many aquatic organisms but may influence the solubility of certain contaminants.

Mineralization, a key indicator of dissolved solids, was measured at 1116.4 mg/l. Elevated levels of mineralization often signify higher concentrations of salts and other dissolved inorganic substances, which can have various implications for aquatic life and potential water usage.

The biochemical oxygen demand (BOD) over a 5-day test period was found to be 8.3 mg/l. This parameter is critical for understanding the organic load in the water, with higher values potentially leading to oxygen depletion and harmful impacts on aquatic organisms. Similarly, the chemical oxygen demand (COD), which measures the total amount of oxygen required to chemically oxidize organic and inorganic matter, was recorded at 36.9 mg/l, providing further insight into the overall pollutant load.

Suspended substances, often indicative of particulate matter, were measured at 24.8 mg/l. These particles can affect water clarity and potentially contribute to the physical stress on aquatic systems.

Key ion concentrations included sulphates at 340.6 mg/l and chlorides at 251.1 mg/l, both of which are common components in wastewater. While these values may not immediately signal toxicity, prolonged exposure at high concentrations can lead to issues such as soil salinization and damage to freshwater ecosystems.

The presence of hydrogen sulfide, albeit at a low concentration of 0.34 mg/l, indicates the occurrence of anaerobic processes, which can generate this gas as a byproduct. Though not immediately hazardous at this level, hydrogen sulfide can cause odor issues and, in higher concentrations, lead to environmental and health concerns.

Nitrogen-based compounds were also observed, with ammonium nitrogen measured at 10.7 mg/l, nitrite nitrogen at 0.8 mg/l, and nitrate nitrogen at 6.3 mg/l. These nitrogen species are crucial for assessing nutrient levels, as excessive amounts can contribute to eutrophication—a process that leads to oxygen depletion and harmful algal blooms in aquatic environments.

Phosphates, another nutrient of concern, were measured at 7.8 mg/l. Like nitrogen compounds, elevated phosphate levels can accelerate eutrophication, which can significantly impair water quality and ecosystem health.

Overall, this analysis provides a comprehensive understanding of the chemical characteristics of wastewater in the Tuzkan storage lake. While the levels of certain substances are within standard environmental thresholds, the presence of nutrients and salts highlights the need for ongoing monitoring and management to prevent potential long-term ecological impacts.

Table 1. Average indicators of the chemical composition of wastewater in the Tuzkan storage lake

Indicators, mg/l	**In the Tuzkan storage lake**
pH value (pH)	8.2
Mineralization, mg/l	1116.4
Biochemical oxygen demand -– 5-day test, mg/l	8.3
Chemical oxygen demand, mg/l	36.9
Suspended substance, mg/l	24.8
Sulphates, mg/l	340.6
Chlorides, mg/l	251.1
Hydrogen sulfi de, mg/l	0.34
Ammonium nitrogen, mg/l	10.7
Nitrite nitrogen, mg/l	0.8
Nitrate nitrogen, mg/l	6.3
Phosphates, mg/l	7.8

The analysis of water balance is a crucial component of wastewater management systems in large storage lakes. In 2024, the water balance of Tuzkan storage lake was studied to better understand its hydrological behavior, the volume of treated water, and how effectively it handles water inflows and discharges.

During the first quarter of 2020, 34,500.012 thousand m³ of water passed through mechanical cleaning processes, followed by biological treatment for 34,000.874 thousand m³. The water was subsequently processed through a divider before admission into Tuzkan storage lake, with no discharge into any rivers. This pattern was consistent throughout the year, with slight variations in water volumes depending on the season. By the end of 2024, a total of 132,551.692 thousand m³ of water had undergone mechanical cleaning, with 49111.87 thousand m³ being directed to Tuzkan storage lake.

Table 2. Results of the analysis of the water balance for Tuzkan in 2024

Quarter	Passed through the mechanical cleaning, thousand m³	Received for biological treatment, thousand m³	Received by the divider, thousand m³	Tuzkan storage lake Admission, thousand m³	For watering, thousand m³	RBSC Admission, thousand m³	RBSC For watering, thousand m³	Discharge into the river, thousand m³
1	34500	34000	32600	26900	610	5875	12753	0
2	32650	31760	23450	16060	615	12745	7450	0
3	32900	32500	13400	17300	618	13300	18740	0
4	32500	32410	30870	11650	620	19145	405	0
Total	132551	130672	100921	49111	618	51050	26640	0

For irrigation purposes, a total of 618.32 thousand m³ was utilized, demonstrating the importance of the lake's water resources for agricultural needs. Simultaneously, approximately 51,050.95 thousand m³ of water was admitted to the RBSC for other industrial purposes. Notably, the lake showed no discharge into adjacent rivers, underscoring its role as a contained system for wastewater treatment.

The results provide a detailed understanding of the water processing capacity of Tuzkan Storage Lake and highlight the importance of effective water treatment processes in managing wastewater inflows.

Wastewater treatment involves multiple stages of purification to ensure that water is clean and safe for both industrial use and irrigation. By the end of 2024, the efficiency of water treatment at Tuzkan Storage Lake had been meticulously evaluated based on key chemical and biological parameters.

The pH levels of the water ranged between 7.4 and 7.6 across different stages of treatment, indicating a neutral to slightly alkaline environment. Suspended substances were reduced from 510.2 mg/l in incoming water to 17.8 mg/l after purification, highlighting the effectiveness of the mechanical cleaning stages.

Nutrient levels, particularly nitrogen compounds, were also carefully monitored. Ammonium nitrogen was significantly reduced from 16.2 mg/l to 6.9 mg/l, while nitrate nitrogen decreased from 9.7 mg/l to 2.49 mg/l. Both reductions play a key role in minimizing the risks of eutrophication in downstream water bodies.

Oxygen demand, both biochemical (BOD) and chemical (COD), were considerably reduced through the treatment process. Biochemical oxygen demand dropped from 463.5 mg/l to 9.5 mg/l, indicating that the organic load in the water was successfully minimized. Similarly, chemical oxygen demand decreased from 947.2 mg/l to 43.2 mg/l, further improving the quality of the treated water.

The study also examined the presence of trace metals and nutrients like iron, calcium, and phosphates. While levels of iron were reduced to 0.43 mg/l and phosphates to 5.9 mg/l, calcium concentrations remained stable within permissible limits for both water storage and irrigation purposes.

The results of these analyses underscore the critical role of Tuzkan storage lake as a comprehensive wastewater treatment system. By adhering to strict water quality standards, the lake effectively supports both agricultural irrigation and industrial usage, contributing to regional water sustainability.

Table 3. Indicators of the quality of cleaning achieved by Tuzkan by 2024

Indicators, mg/l	Incoming water	Clarified water	Purified water	Maximum permissible discharges to Tuzkan storage and RBSC storage	Maximum permissible discharges for irrigation
pH value (pH)	7.4	7.5	7.6	6–9	pH≤5.0
Suspended substance, mg/l	510.2	115.5	17.8	28.0	10.0
Ammonium nitrogen, mg/l	16.2	13.6	6.9	18.5	5.0
Nitrite nitrogen, mg/l	0.12	0.13	0.62	1.8	3.5
Nitrate nitrogen, mg/l	9.7	2.3	2.49	5.1	45.5
Biochemical oxygen demand — 5-day test, mg/l	463.5	135.2	9.5	9.8	10.5
TBOD, mg/l	839.1	200.2	12.7	17.0	12.5
Chemical oxygen demand, mg/l	947.2	251.3	43.2	33.0	3.8
Iron, mg/l	2.12	0.45	0.43	2.6	0.5
Calcium, mg/l	65.4	61.2	58.5	100.0	150.5
Phosphates, mg/l	10.5	8.1	5.9	35.0	3.5
Chlorides, mg/l	85.7	74.2	52.9	101.0	350.5
Zinc, mg/l	0.03	0.017	0.013	0.09	0.15
Mineralization, mg/l	605.82	559.21	441.93	2000.0	2100.0

Here is a revised conclusion integrating the key points from the three articles:

Conclusion

The analysis of existing technologies for the removal of heavy metal ions from wastewater highlights the need for the development of innovative treatment methods based on principles of physical chemistry. These new technologies should adhere to the current requirements for an integrated approach to wastewater treatment. It is crucial that the treated wastewater meets standards that allow its reuse for industrial and technical applications or its safe discharge into municipal sewer systems. Furthermore, the sludge produced during treatment should be either low-toxic or a material that can be repurposed as secondary raw material for other industrial processes or transformed into a final marketable product.

The study of the Tuzkan storage lake's water balance and treatment efficiency for 2024 emphasizes the significance of effective water management practices in achieving these goals. Water quality analysis revealed substantial reductions in suspended substances, nutrients, and oxygen demand, ensuring that the treated water is suitable for reuse in irrigation and industrial processes. Moreover, maintaining safe levels of key pollutants, such as ammonium nitrogen and trace metals, is essential in preventing environmental degradation and promoting sustainability.

In line with the integrated wastewater management approach, the advanced treatment technologies employed at Tuzkan storage lake demonstrate a successful model for minimizing the environmental impact of wastewater discharge while enabling resource recovery. The continuous monitoring and optimization of treatment processes are critical for ensuring that water and sludge are treated to the highest standards, thus contributing to the broader objectives of water sustainability and circular economy practices.

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